

Impact of SO₂-poisoning over the lifetime of a Cu-CHA catalyst for NH₃-SCRPeter S. Hammershøj^{a,b}, Anker D. Jensen^b, Ton V.W. Janssens^{a,*}^a Umicore Denmark ApS, Nøjsomhedsvej 20, 2800 Kgs. Lyngby, Denmark^b Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads B229, 2800 Kgs. Lyngby, Denmark

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ABSTRACT

Cu-CHA catalysts for NH₃-SCR in exhaust after treatment systems of heavy-duty vehicles, are constantly exposed to SO₂ during their lifetime of about 10,000 h. In order to study the development of deactivation by SO₂, a Cu-CHA catalyst was exposed to SO₂ at 200, 300, 400 and 500 °C for different durations up to 120 h, resulting in total SO₂ exposures that are comparable to that of the lifetime of a Cu-CHA catalyst in an after treatment system. The measured deactivation increases very fast to a steady level in the range 0.85–0.95, dependent on the exposure temperature, which shows the need for frequent regeneration of the catalyst. Regeneration at 550 °C can restore the activity of the catalyst to 80% of its fresh activity level even after 120 h exposure, suggesting frequent regeneration as a feasible method for overcoming SO₂-poisoning. ICP analyses showed that SO₂ exposure led to S/Cu ratios in the range 0.5–1, indicating that sulfur is associated with Cu. After regeneration the S/Cu ratios did not exceed 0.2, suggesting that only certain Cu sites are able to form Cu₂S species that are thermally stable above 550 °C. This together with the observations that the deactivation before and after regeneration impact differently on the activation energy of the SCR reaction, and that the deactivation never exceeded 0.95, suggests that SO₂-poisoning of Cu-CHA depends on the structural properties of this material. TGA measurements of the mass uptake during SO₂ exposure was consistent with a process where SO₂ is initially adsorbed on Cu, and then slowly oxidized to SO₃ at 200 °C, whereas the mass uptake at 500 °C was consistent with an immediate adsorption of SO₃, which is accredited to a faster oxidation rate at higher temperature.

1. Introduction

Combustion engines in vehicles produce polluting compounds, and their emissions are restricted by legislation. In particular, the emissions of NO_x (NO and NO₂) from vehicles is strictly regulated, which already has resulted in a significant improvement of air quality [1]. For diesel engines, the most effective method to reduce NO_x emissions to the levels required by legislative regulations, is by selective catalytic reduction with NH₃ (NH₃-SCR), and modern diesel exhaust aftertreatment systems contain one or more catalytic converters for NH₃-SCR [2].

A widely used technique for dosing of NH₃ in exhaust aftertreatment systems is by injection of aqueous urea, which decomposes to NH₃ above 180 °C [2], setting a lower temperature limit for NH₃-SCR in an exhaust system. Furthermore, the improved fuel efficiency of diesel engines that has been achieved in recent years, in order to lower the CO₂ emissions, has resulted in colder exhaust gas. Consequently, it takes longer time to heat the catalysts in the exhaust aftertreatment system, and therefore, the low-temperature activity, in particular around 180 °C, has become more important for the abatement of NO_x emissions.

Currently employed SCR catalysts are V₂O₅-based or zeolites containing Fe or Cu. Especially Cu-zeolites of the CHA topology are very active in the low-temperature range 180–300 °C, which in combination with their high hydrothermal stability and low N₂O selectivity, has made these materials particularly interesting as SCR catalysts for automotive applications [2–4]. The Al centers in the zeolite framework generates locations with negative charge, which are balanced by external cations. In the case of Cu-CHA, Cu in these ion-exchange positions gives rise to the activity of the Cu-CHA catalysts for the NH₃-SCR reaction. Cu-CHA catalysts have two characteristic activity regimes, namely a low-temperature (approx. 200–300 °C) and a high-temperature (> 350 °C) [5], which are separated by a region where the steady state NO_x conversion actually can decrease with increasing temperature [6]. The low-temperature activity of Cu-CHA catalysts is ascribed to the formation of mobile [Cu(NH₃)₂]⁺ complexes in the presence of NO and NH₃, which enables formation of Cu pairs that efficiently dissociate O₂ [7–14], which is a key step in the NH₃-SCR reaction.

A drawback of Cu-zeolite catalysts is their sensitivity to SO₂. SO₂ is formed by oxidation of sulfur-containing compounds in the fuel and engine lubrication oils. In practice, the formation of SO₂ is limited by

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reduction of the sulfur content in diesel fuels, and therefore, the use of ultra-low sulfur diesel (ULSD) has been implemented in USA and Europe. The current maximum allowable sulfur concentration in ULSD is 15 wt ppm in USA and 10 wt ppm in Europe [1]. The use of ULSD results in a typical SO₂ concentration in the exhaust gas in the range 0.5–2 volume ppm SO₂. Even at such low SO₂ concentrations, a considerable deactivation of Cu-CHA catalysts, particularly in the low-temperature regime, is still observed [6,15–22].

The differences in the effect of SO₂ on the performance of the different types of NH₃-SCR catalysts is clearly related to the chemistry of the systems [22]. The high SO₂ sensitivity for Cu-zeolites, compared to Fe-zeolites, is possibly due to the higher stability of Cu-sulfate compared to Fe-sulfate [23]. This is consistent with the observed release of SO₂ and restoration of activity of Cu-CHA by heating to 700 °C, which is above the temperature for thermal decomposition of Cu-sulfate [6,18,22,23]. This suggests that the deactivation induced by SO₂ is at least partially due to the formation of some SO₃. In an aftertreatment system, SO₃ can form from oxidation of SO₂, which can take place over the diesel oxidation catalyst and also in the Cu-CHA catalyst itself [6,15,18,20]. Therefore, to understand the deactivation of Cu-zeolite catalysts by SO₂, the formation and interaction of SO₃ with Cu must be considered as well. This means that the SO₂-induced deactivation of Cu-zeolites is influenced by many factors, such as temperature, gas environment, and oxidation of SO₂ to SO₃ [6,15,18,22], and several Cu₂S species of varying stability that can be formed [6,15–18,22,24,25].

A potentially feasible method for treating SO₂-induced deactivation of Cu-CHA catalysts in an exhaust system is by thermal regeneration of the catalyst, which is possible due to the different stabilities of the Cu₂S species [6,15,18,20,22,26]. In a typical modern aftertreatment system, an achievable maximum temperature of the SCR catalyst for regeneration is about 550 °C. Regeneration of a Cu-CHA catalyst at this temperature reverses the predominant part of the deactivation [6]. Thus, the total deactivation measured after exposure to SO_x can be divided into a reversible and an irreversible part, by measuring the irreversible deactivation after regeneration at 550 °C [6].

The required lifetime of an SCR catalyst in an aftertreatment system of a heavy-duty diesel vehicle is about 10,000 h. Throughout its lifetime, the SCR catalyst is constantly exposed to low concentrations of SO₂, which makes the deactivation a continuous process persisting over the lifetime of the catalyst. Therefore, it is important to know the impact of these low SO₂ concentrations over long-term SO₂ exposure. The deactivation process can be accelerated by increasing the SO₂ concentration [22], because the deactivation appears to depend on the total SO₂ exposure [22], defined as the product of the SO₂ concentration and the exposure time. In this way, the development of the reversible and irreversible deactivation over the lifetime of the catalyst can be assessed from experiments of significantly shorter exposure times, but with higher SO₂ concentrations.

In this contribution, the deactivation and regeneration of a Cu-CHA catalyst is investigated for SO₂ exposures of increasing duration up to 120 h and with 50 ppmv SO₂, which is comparable to the total SO₂ exposure of a commercial Cu-CHA SCR catalyst during its required lifetime. The deactivation is evaluated by comparing the performance of the catalysts in the NH₃-SCR reaction after SO₂ exposure at 200–500 °C, and after regeneration at 550 °C, to that of the fresh. This is important, in order to assess the impact of the reversible and irreversible deactivation development over long-term SO₂ exposure. Furthermore, the catalytic performance is compared to the S uptake of the catalysts exposed at 200–500 °C, as determined by ICP, and to in situ thermogravimetric measurements of SO₂ exposure at 200 and 500 °C.

2. Experimental

The zeolite material used in this study is a CHA zeolite with a Si/Al ratio of 14.6. Cu was introduced in the zeolite by mixing it with the

appropriate amount of an aqueous Cu(NO₃)₂ solution to obtain 2.5 wt% Cu in the zeolite. After mixing, the slurry was dried at 120 °C and calcined at 550 °C for 3 h. The calcined catalyst powder was light blue, indicating that Cu is located in the ion-exchange positions of the CHA material. The Si, Al and Cu content were determined by ICP-OES to be 37.5, 2.46, and 2.43 wt%, respectively, corresponding to a Cu/Al ratio of 0.42, and estimated 2.76 wt% Cu on a dry matter basis.

The SO₂ exposures were carried out in a flow reactor setup, equipped with 4 parallel quartz reactor tubes, each with independent control of the temperature. A sample of 1.6 g of fresh catalyst powder (sieve fraction 150–300 μm) was added to each reactor tube and held in place by quartz wool plugs. Prior to SO₂ exposure, all catalyst loadings were heated to 500 °C for 2 h in a flow of 10% O₂, 5% H₂O, and sufficient N₂ to obtain a total flow rate of 1.67 NL/min. Then, one reactor was kept at 500 °C, and the other three reactors were cooled to 200, 300, and 400 °C. For the SO₂ exposure, 50 ppmv SO₂ was added to the reactor feed, while keeping the same total flow rate. In 6 different runs, the duration of SO₂ exposure was varied and chosen as 1, 5, 15, 30, 65, 120 h. In this way, a total of 24 catalyst samples were obtained, each with different SO₂ exposure duration and temperature. Finally, 0.8 g of each of these 24 samples was regenerated in the same parallel reactor setup by exposing to 550 °C for 6 h in a flow of 10% O₂, 5% H₂O, and N₂ to balance the flow to 1.67 NL/min.

This yields a total of 48 treated catalyst samples, 24 exposed to SO₂ and 24 regenerated, which were all analyzed for Cu and S content using ICP-OES in order to determine the S/Cu ratio after each treatment of the catalyst.

The NH₃-SCR activity measurements were done in a microreactor setup, by adding 5 mg (dry matter basis) catalyst powder, 150–300 μm sieve fraction, to a quartz U-tube reactor with an inner diameter of 2 mm, using quartz wool to keep the catalyst in place. The reactor feed gas consisted of 500 ppmv NO, 533 ppmv NH₃, 10% O₂, 5% H₂O, in N₂ at a total flow rate of 225 N mL/min. To measure the NH₃-SCR activity, the catalyst was heated stepwise to 160, 180, 190, 200, 210, 220, 250, 300, 325, 350, 400, and 550 °C and kept at these temperatures for 40 min to ensure stationary conditions. The concentrations of NO, NH₃, NO₂, and N₂O in the reactor exit gas were monitored continuously by a Gasmet CX4000 FTIR analyzer, connected to the reactor outlet. The feed gas concentrations were measured by bypassing the reactor, using the same FTIR analyzer.

To determine the NH₃-SCR activity, the steady state conversion was determined from the activity measurement, and converted to a rate constant according to:

$$k = -\frac{F}{W} \ln(1-X) \quad (1)$$

where F is the total molar flow rate, W is the catalyst mass, and X is the NO conversion. For the deactivation we use our earlier definition [6] in which the rate constants of the catalysts exposed to SO₂ before or after regeneration (k) are related to the corresponding rate constant of the fresh catalyst (k_{fresh}), as expressed in:

$$\text{Deactivation} = 1 - \frac{k}{k_{\text{fresh}}} \quad (2)$$

Finally, the uptake of sulfur at 200 °C and 500 °C was followed by thermogravimetric analysis (TGA) in two separate measurements. For these measurements, a sample of the fresh catalyst was heated to 550 °C for 1 h in 10% O₂ in N₂, at a total flow rate of 150 N mL/min, to obtain the dry mass of the catalyst. The dry masses of the samples used were 25.9252 mg (S uptake at 200 °C) and 37.6135 mg (S uptake at 500 °C). Then, the catalyst was exposed to SO₂ at 200 °C or 500 °C, using a feed gas consisting of 50 ppmv SO₂, 3% H₂O and 10% O₂ in N₂, also at a total flow rate of 150 N mL/min, while monitoring the change in catalyst mass. Changes in catalyst mass during regeneration were obtained by heating to 550 °C and changing the feed gas to 10% O₂ in N₂, while keeping the same total flow rate. The changes in S uptake are

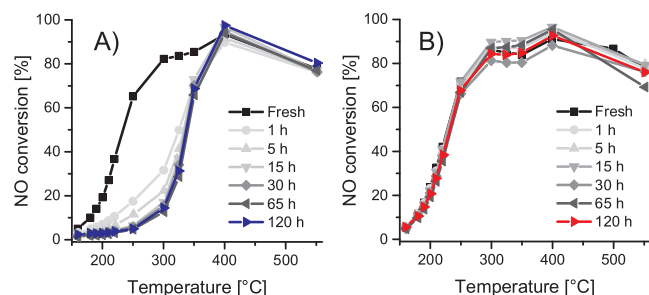


Fig. 1. Steady state NO conversions plotted as function of the temperature in the NH₃-SCR reaction over A) the SO₂ exposed catalysts, and B) the regenerated catalysts. The measurements were carried out with inlet concentrations of 500 ppmv NO, 533 ppmv NH₃, 10% O₂, 5% H₂O and N₂ to a total flow rate of 225 N mL/min.

determined from the weight changes in alternating SO₂ exposure and regeneration phases at a fixed temperature (200 or 500 °C), where catalysts are regenerated after the same cumulative durations of the SO₂ exposure as used in the deactivation measurements given above.

3. Results

Fig. 1 shows the development of the steady state NO conversions as function of the temperature over the duration of exposure to SO₂ at 200 °C, and after subsequent regeneration by heating at 550 °C for 6 h. In all cases, the NO conversion in the temperature range 160–350 °C is considerably lower after exposure to SO₂, compared to the fresh catalyst. Regeneration at 550 °C mostly restores the NO conversion in that temperature range. The same trends are observed after exposure to SO₂ at 300 °C, 400 °C, and 500 °C, see supporting information. This behavior can be described in terms of reversible and irreversible deactivation as defined earlier [6]. The deactivation remaining after regeneration is then the irreversible deactivation, and the reversible deactivation is defined as the difference in deactivation of the SO₂ exposed catalyst before and after regeneration [6].

The total SO₂ exposure, which corresponds to the product of the exposure time and SO₂ concentration, appears to be a good descriptor for deactivation by SO₂ [22], which also allows for estimation of the deactivation over the entire required lifetime of the catalyst. Fig. 2 summarizes the development of the reversible and irreversible deactivation with SO₂ exposure for the exposure temperatures of 200, 300, 400, and 500 °C, along with the corresponding S/Cu ratio measured by ICP. Both the reversible and irreversible deactivation initially show a fast increase with SO₂ exposure, and reach a final level after an SO₂ exposure of 500–1000 ppm h, after which the deactivation remains constant. It is noted that the predominant part of the final deactivation level is reached already after 50 ppm h, which is the first data point in each SO₂ exposure series, indicating that the effect of SO₂ is almost immediate. The final deactivation after SO₂ exposure, before regeneration, is 0.85–0.95 and depends on the temperature of SO₂ exposure. The irreversible deactivation is about 0.2–0.3, independent of the temperature for SO₂ exposure. It is also noted that we have not found any conditions in which a complete deactivation of the Cu-CHA is observed.

In order to relate the measured deactivation of the Cu-CHA catalyst with the sulfur uptake, the deactivation is compared to the measured S/Cu ratios before and after regeneration. The S/Cu ratios of the regenerated states of the catalyst mirrors the observed irreversible deactivation, with a rapid increase during the first 1000 ppm h SO₂, followed by a constant final level of about 0.2, independent of the temperature of SO₂ exposure. This value matches the observed deactivation level of 0.2–0.3 quite well, suggesting that the irreversible deactivation is related to the adsorption of sulfur on the active Cu sites.

The measured S/Cu ratios before regeneration do not appear to

reach a final level. The S/Cu ratios initially increase fast, which parallels the fast increase of the deactivation, but after about 1000 ppm h SO₂, the S/Cu ratio continues to increase at a lower rate, except for the catalysts exposed to SO₂ at 500 °C. The measured S/Cu ratios are, in most cases, lower than the observed levels of deactivation, which indicates that the reversible deactivation cannot be directly explained by Cu site blocking with sulfur. Nevertheless, the observation that the S/Cu ratios generally are lower than 1 indicates that the uptake of sulfur is related to the Cu and is consistent with adsorption of sulfur on Cu.

A more detailed comparison of the measured S/Cu ratios and the reversible and irreversible deactivation, is shown in Fig. 3. The reversible deactivation is always disproportionately larger than the corresponding S/Cu ratios, while the irreversible deactivation generally is closer to a 1:1 correlation with the S/Cu ratio, which would be expected for deactivation by single site blocking. This shows that the impact of sulfur uptake on the reversible deactivation is larger compared to the irreversible deactivation. This also suggests that the reversible and irreversible deactivation are related to the formation of different Cu₂S species or selective adsorption of sulfur on specific Cu-sites.

The difference between reversible and irreversible deactivation is also reflected in the apparent activation energy for the NH₃-SCR reaction. Fig. 4 shows the apparent activation energies for the different SO₂ exposures before and after regeneration. Clearly, for the catalysts before regeneration, the activation energy is lowered from about 70 kJ/mol to about 30 kJ/mol for an SO₂ exposure of about 1000 ppm h, which coincides with the observed fast increase in deactivation and initial uptake of sulfur. At longer SO₂ exposures, the apparent activation energy remains constant. For the regenerated catalysts, all measured activation energies are about 70 kJ/mol, which is close to the value of the fresh catalyst, independent of SO₂ exposure time or temperature. This means that the level of deactivation of the Cu-CHA catalyst by SO₂ is not only the result of a certain amount of S in the catalyst, but also depends on which Cu₂S species that are present. The different trends observed for the activation energies before and after regeneration are also an indication of different mechanisms for the SCR reaction on the reversibly and irreversibly deactivated Cu-CHA catalysts, in agreement with an earlier conclusion [6].

The different influence of the SO₂ exposure temperature on the sulfur uptake related to the reversible or irreversible deactivation is illustrated in Fig. 5, which shows the measured S/Cu ratios as function of the exposure temperatures. As also noted above, the S/Cu ratios related to the irreversible deactivation reach approximately 0.2 for all exposure temperatures, which suggests that the irreversible deactivation is related to the formation of a Cu₂S species at certain Cu sites. The S/Cu ratios related to the reversible deactivation in Fig. 5 show a maximum sulfur uptake at 400 °C for short SO₂ exposure (1 and 5 h), and at 300 °C for the longer SO₂ exposures. This trend is similar to that observed on a Cu-SAPO-34 catalyst exposed to SO₂ in O₂ and H₂O at different temperatures [22], and reflects a trade-off between the kinetics of the formation of the Cu sulfate species and the equilibrium adsorption concentration [22].

TGA measurements were used to assess the sulfur uptake during SO₂ exposure at 200 °C and 500 °C in more detail, to better understand the effect of SO₂ at low and high temperature. Fig. 6 shows how the relative mass of the catalyst (with the dry mass of the catalyst before SO₂ exposure as basis) changes with the total SO₂ exposure. Both at 200 °C and 500 °C, SO₂ exposure leads to a steep increase in the catalyst mass at SO₂ exposures below 500 ppm h. At 500 °C, a relative mass of 1.02 is reached, which remains stable after longer exposures to SO₂, while at 200 °C, the relative mass initially increases to 1.01, which then increases further to approximately 1.03 after 6000 ppm h SO₂ exposure. This is qualitatively the same trend as found for the S/Cu ratio (Fig. 2), which is an indication that the observed increase in catalyst mass is indeed due to the uptake of SO₂.

For a more precise interpretation of the observed increase in catalyst mass upon exposure to SO₂ at 200 °C and 500 °C, we need to know in

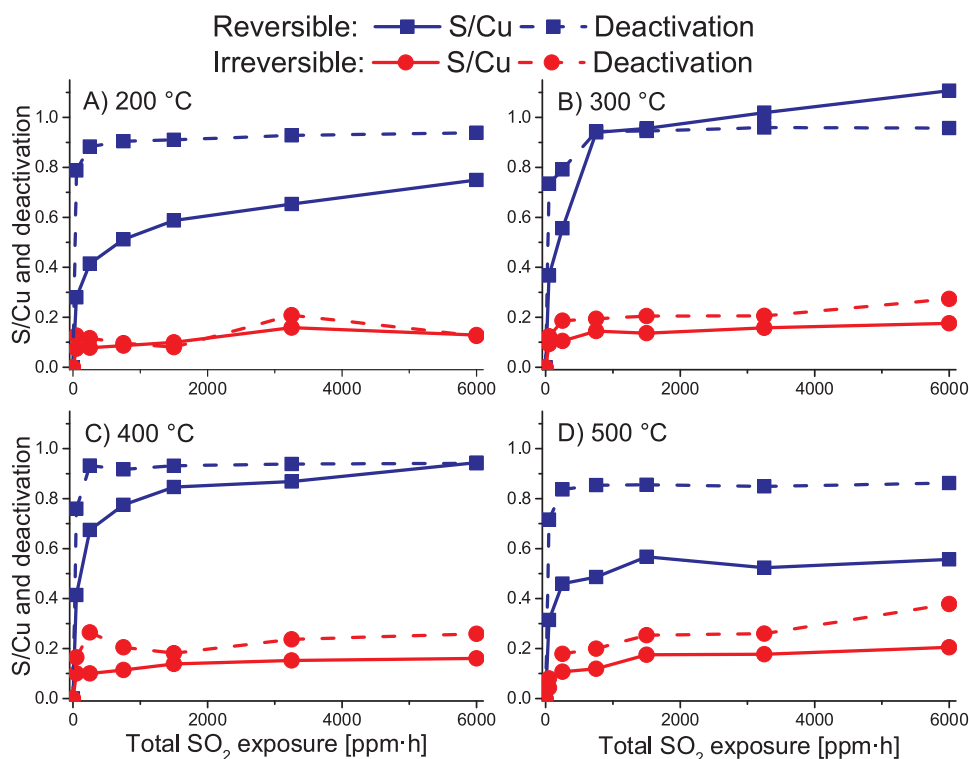


Fig. 2. Reversible (squares) and irreversible (circles) deactivation at 220 °C (dashed lines), and S/Cu ratios (solid lines), plotted as functions of the total SO₂ exposure, for the catalysts exposed to SO₂ at A) 200 °C, B) 300 °C, C) 400 °C, and D) 500 °C, and for the corresponding regenerated catalysts.

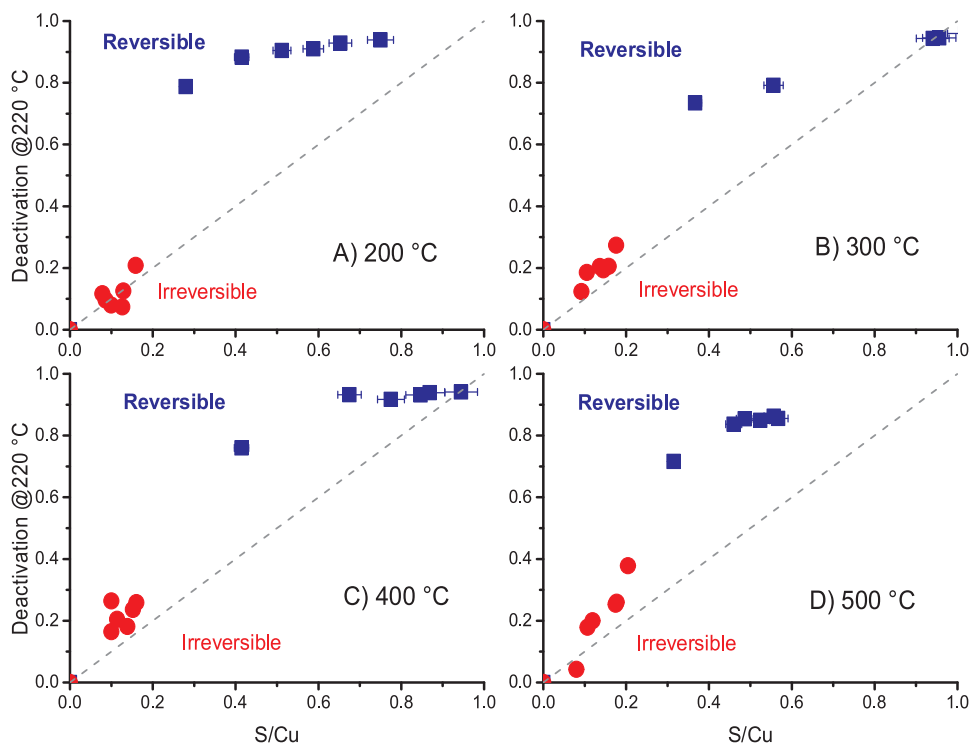


Fig. 3. Reversible (squares) and irreversible (circles) deactivation at 220 °C plotted as functions of the S/Cu ratios for the exposure temperatures A) 200 °C, B) 300 °C, C) 400 °C, and D) 500 °C.

which form the SO₂ is adsorbed on the catalyst. The most obvious options are adsorption of SO₂ or SO₃, and the formation of sulfites and sulfates on the Cu sites [6,15,16,18,22]. By comparing the observed increases in catalyst mass measured in the TGA experiments with the measured S/Cu ratios given in Figs. 2 and 5, it is possible to work out

whether the sulfur is adsorbed as SO₂ or SO₃. First, the observed increase in catalyst mass is converted to a molar amount of sulfur, under the assumption that the sulfur is present as either SO₂ or SO₃, which together with the known Cu content, 2.76 wt% on dry matter basis, results in an estimated SO₂/Cu and SO₃/Cu ratio. In Fig. 7, these

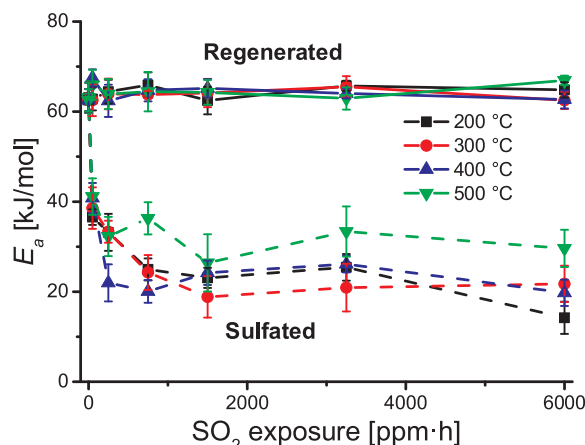


Fig. 4. Activation energies in the NH_3 -SCR reaction for the SO_2 exposed (dashed lines) and regenerated (solid lines) catalysts, plotted as functions of the total SO_2 exposure.

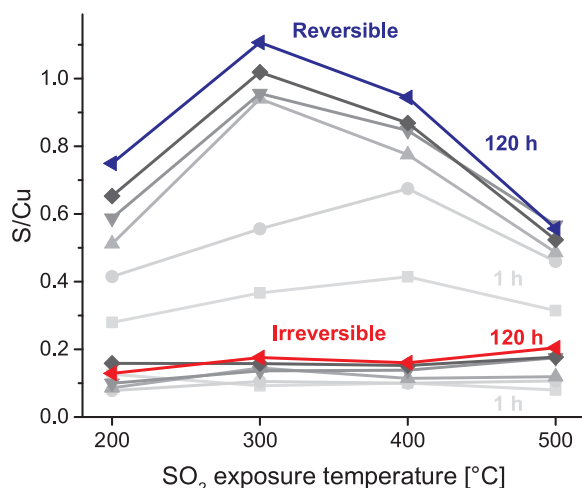


Fig. 5. Development of the reversible and irreversible S/Cu ratios from 1 h to 120 h of SO_2 exposure, plotted for each exposure temperature.

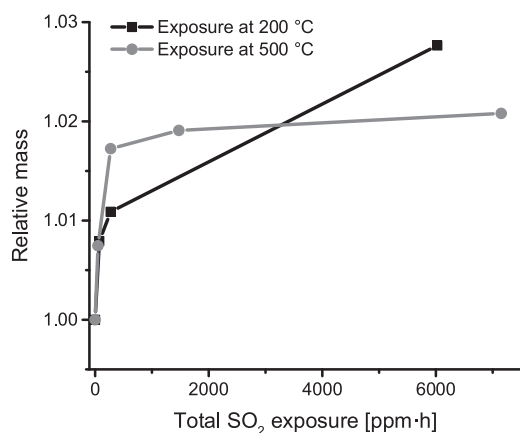


Fig. 6. Relative masses of the catalysts exposed to SO_2 at 200 °C (black) and 500 °C (grey) in the thermogravimetric setup, plotted as functions of the total SO_2 exposure.

estimated SO_2/Cu and SO_3/Cu ratios are compared to the measured S/Cu ratios determined by ICP, for Cu-CHA exposed to SO_2 at 200 °C and 500 °C. At an SO_2 exposure temperature of 200 °C, the SO_2/Cu ratios follow the measured S/Cu ratios to 1000 ppm·h of SO_2 exposure. At

6000 ppm·h SO_2 , the measured S/Cu ratio matches the estimated SO_3/Cu ratio. This indicates that initially it is SO_2 that is adsorbed on the Cu, but it is slowly oxidized to SO_3 . With an SO_2 exposure temperature of 500 °C, the estimated SO_3/Cu ratio matches the S/Cu ratio over the entire SO_2 exposure duration. This clearly shows that at 500 °C, oxidation of SO_2 is faster, and adsorption is essentially as SO_3 . Adsorption of SO_3 on a Cu-OH species actually corresponds to the formation of a bisulfate species, which have been proposed earlier as being the cause of the irreversible deactivation [6,15,16,18–22,24,25].

4. Discussion

The results presented above clearly show that SO_2 primarily affects the low-temperature activity of Cu-CHA catalysts for SCR, and therefore, the impacts of SO_2 on the high-temperature activity will not be discussed further here.

For an SCR catalyst that has a required lifetime of about 10,000 h, it is important to be able to estimate the performance for the entire lifetime. One way to do this is by comparison of the total SO_2/Cu exposure for the lifetime of the catalyst in a heavy-duty vehicle to similar conditions in a test. The total SO_2/Cu exposure for a Cu-CHA catalyst over its lifetime is about 44, assuming that the vehicle covers 800,000 km with a consumption of 30 L/100 km, using 5 wt ppm S diesel, and with a Cu-loading of 45 g of the Cu-CHA SCR catalyst. The total molar SO_2/Cu exposure in the experiments presented in this article is 41.7 after 120 h, which is similar to the typical SO_2/Cu exposure in an exhaust system. Therefore, we expect that the development of SO_2 -poisoning in our experiments reflect that of a Cu-CHA SCR catalyst in an exhaust after-treatment system.

The results presented in this study shows that the reversible deactivation increases fast to a high level, independent of the SO_2 exposure temperature. This means that the SCR catalyst in an exhaust system requires frequent regeneration in order to maintain an efficient NH_3 -SCR performance, especially in the context of cold start where the low-temperature activity is particularly important. Based on the presented results, it is actually possible to restore the predominant part of the original activity of the catalyst throughout its lifetime, by regeneration at 550 °C. This shows that SO_2 -poisoning of Cu-CHA catalysts is occurring over the lifetime of the catalyst, but that it can be managed by proper regeneration strategies. Furthermore, the irreversible deactivation seems sufficiently small to be handled by appropriate system design.

The use of Cu-CHA catalysts in exhaust systems appears to rely on the efficiency of regeneration, which likely depends on the SO_2 concentration during regeneration. Thus, exposure to 50 ppmv SO_2 at 500 °C leads to uptake of sulfur by the catalyst, while regeneration at 550 °C in the absence of SO_2 partially removes sulfur from the catalyst. Furthermore, reversible and irreversible deactivation of a Cu-SAPO-34 catalyst have been shown to build up when exposed to SO_2 concentrations as low as 1.5 ppmv at 500 °C [22]. Therefore, it appears that the uptake or removal of sulfur depends on the SO_2 concentration being above or below a critical value, which is somewhere in the range 0–1.5 ppmv SO_2 . This could potentially complicate the regeneration if the SO_2 content of the exhaust gas is above the critical concentration, in which case a regeneration would resemble the SO_2 exposure at 500 °C. In that case, the low-temperature activity of Cu-CHA catalysts would be lost relatively fast, and so would the main advantage of using these materials compared to Fe-zeolites or vanadia-based systems. The efficiency of regeneration, and the critical SO_2 concentration, would have to be verified in an actual exhaust system, since reducing compounds in the exhaust gas, such as hydrocarbons and NH_3 , have been shown to have a beneficial effect for removing sulfurous compounds from Cu-CHA catalysts [26].

The process for the uptake of sulfur by the Cu-CHA catalyst possibly proceeds by an initial adsorption of SO_2 on Cu where the sulfur is subsequently oxidized to sulfate. This is envisioned because the Cu-CHA

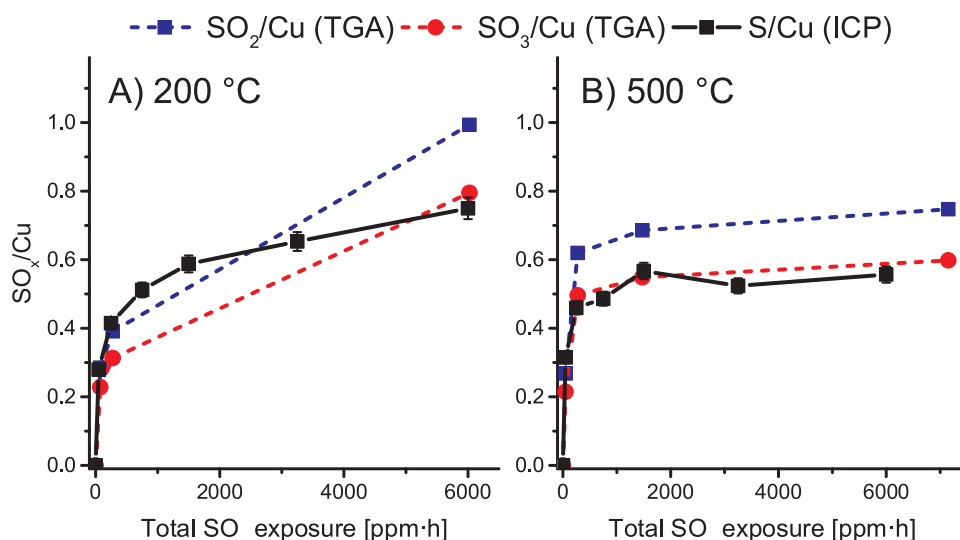


Fig. 7. SO_x/Cu ratios plotted as functions of the total SO_2 exposure for catalysts exposed to SO_2 at A) 200 °C, and B) 500 °C. Black solid lines are S/Cu ratios determined by ICP-OES on catalysts exposed to SO_2 in the reactor setup. Dashed lines are SO_2/Cu ratios (blue squares) and SO_3/Cu ratios (red circles) based on the mass increase measured in the thermogravimetric setup. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

catalyst is exposed to SO_2 , which must oxidize in order to constitute the forms of sulfate that are associated with the Cu_2S species causing the reversible [6,15,16,18,22] and irreversible deactivation [6,22]. The proposed process is consistent with the results from the TGA experiment at 200 °C (Fig. 7), where the initial mass uptake fits with an uptake of SO_2 , and over time changes to fit better with an uptake of SO_3 . At this temperature (200 °C), there is a clear difference between the initial and final uptake, which indicates that the oxidation of SO_2 is kinetically controlled. In the TGA experiment at 500 °C, the mass uptake fits with a constant uptake of SO_3 , which can be explained by a faster oxidation of SO_2 at this temperature [20,22], which both could be on the Cu sites or in the gas phase.

A possible reason for the disproportionately high reversible deactivation, as compared to the S/Cu ratio, is that the adsorption of SO_2 affects the mobility and effective amount of $[\text{Cu}(\text{NH}_3)_2]^+$ ions in the Cu-CHA zeolite. The current understanding of the low-temperature part of the SCR mechanism is that the mobile $[\text{Cu}(\text{NH}_3)_2]^+$ complexes allow for the formation of pairs of Cu ions, which are crucial for the dissociation of the oxygen molecules [8,11]. As a consequence, the activity depends on the square of the Cu density below a certain Cu loading, and depends linearly on the Cu density above it [8]. This results in two distinct activity regimes, which may be related to the different impacts of the sulfur loading on the reversible and irreversible deactivation. In principle, the mechanism based on mobile $[\text{Cu}(\text{NH}_3)_2]^+$ complexes implies that all Cu sites are the same, namely the mobile $[\text{Cu}(\text{NH}_3)_2]^+$ complex, and contribute equally to the activity. Ultimately, the activity is determined by the amount of Cu pairs that are formed at the given conditions. The different trends for the activation energy of the SCR reaction with reversible and irreversible deactivation, as shown in Fig. 4, and the disproportionately larger reversible deactivation than irreversible deactivation as compared to the S/Cu ratios shown in Fig. 3 can be understood in relation to the two activity regimes. Since the S/Cu ratios related to the irreversible deactivation are always lower than those related to the reversible deactivation, and lower than 0.2, the amount of deactivated Cu in these cases may be sufficiently small to keep the amount of non-deactivated Cu in the linear dependence regime. The activity is then not limited by formation of Cu pairs, and the deactivation would simply correspond to a loss of active sites, which is also consistent with the values of the activation energies close to that of the fresh catalyst. For the reversible deactivation, the S/Cu ratios of 0.3–1 could enforce a situation where the effective Cu content becomes sufficiently low for the activity to be restricted by formation of Cu pairs. In this situation, the activity depends on the square of the effective Cu density, and therefore, it would be expected that the deactivation is disproportionately larger than the S/Cu ratio, as observed in Fig. 3. The

lower activation energy is then related to the fact that the rate of the SCR reaction is determined by the limited rate of Cu pair formation.

The observation that similar sulfur contents can result in significantly different levels of reversible and irreversible deactivation [6] is not consistent with the idea that all Cu sites contribute equally to the rate of the NH_3 -SCR reaction. Factors like the zeolite structure and Al distribution can also influence the reactivity or mobility of Cu, eventually resulting in Cu sites of different activity. This idea is supported by two observations of the SO_2 exposed and regenerated Cu-CHA catalyst in Fig. 2. The first observation is that the reversible deactivation never exceeds 0.95, indicating that some Cu does not adsorb SO_2 or is not affected by SO_2 , and the second observation is that the S/Cu ratio related to the irreversible deactivation is limited to 0.2, suggesting that the more stable Cu sulfate species can only form at certain Cu sites. According to this view, the deactivation and regeneration behavior of Cu-CHA catalysts also depend on the structural properties of the catalyst.

5. Conclusion

A Cu-CHA catalyst for NH_3 -SCR has been exposed to SO_2 at different temperatures in the range 200–500 °C, and at durations up to 120 h, resulting in a total SO_2 exposure that is similar to what an SCR catalyst experiences over the entire lifetime in an exhaust aftertreatment system on a heavy-duty vehicle. Activity measurements after SO_2 exposure, and after regeneration at 550 °C, enabled measurement of the extent of deactivation of the catalyst in these two states. The deactivation of the low-temperature activity of the Cu-CHA catalyst in the presence of SO_2 occurs fast in the entire temperature window 200–500 °C to a final deactivation level in the range 0.85–0.95, dependent on the exposure temperature. Heating in SO_2 -free gas to 550 °C restores the activity to about 80% of its original level, even after a total S/Cu exposure similar to that of the lifetime of a Cu-CHA SCR catalyst in a heavy-duty diesel after treatment system. This suggests regeneration as a feasible method for handling SO_2 -poisoning, since proper dimensioning of the catalyst easily can treat the irreversible deactivation of maximum 0.2–0.3 that develops over long-term SO_2 exposure.

Analogous to the deactivation, the S/Cu ratios also increase fast initially, and the S/Cu ratios of the SO_2 exposed catalysts reach different levels in the range of 0.5–1, dependent on the exposure temperature. The regenerated S/Cu ratios never exceed 0.2, indicating that the irreversible Cu₂S species are restricted to certain Cu sites. The mechanism of the sulfur uptake appears to proceed by an initial uptake of SO_2 by the catalyst, followed by oxidation to sulfate on the catalyst, at a rate that increases with temperature.

The reversible and irreversible deactivation have a different impact on the low-temperature SCR mechanism, which is seen by i) a disproportionately larger reversible deactivation relative to the S/Cu ratio as compared with the irreversible deactivation, and ii) by the reversible deactivation causing a change in the activation energy of the SCR reaction, whereas the irreversible deactivation does not. This, together with the observations of a maximum irreversible S/Cu ratio of 0.2, and a maximum deactivation level of 0.95, points to a dependence of the SO₂-poisoning of Cu-CHA catalysts on structural properties of the Cu-CHA material.

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Declarations of interest

None.

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